

## TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX OF WATER-ETHANOL SYSTEM

### Part IV.—Measurements on the Activation Energy of Viscous Flow for Aqueous Ethanol Solutions from 11% to 24% at Intervals of 2.5% Ethanol

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The detailed study of the activation energy of viscous flow ( $E_\eta = -T^2 \Delta \ln \eta / \Delta T$ ) is now extended to concentrations from 11% to 24% ethanol. The measurements are made at intervals of 1°C on solutions whose concentrations differ by 2% to 3% ethanol. The temperature positions of the various jumps, classified as small, medium or large, can be readily connected by smooth curves, which link up with the earlier graphs for the range of 0% to 5% ethanol.

Some of the energy jumps are found to show subsidiary steps that grow in size as the concentration changes. Many such anomalous branchings are observed at concentrations lower than 6%, whereas the region from 11% to 16% shows a remarkable degree of stability. It appears probable that there are several significant structural changes corresponding to the branching out of these energy jumps, and finer studies in the range of 0% to 5% ethanol are in hand to elucidate this further.

### Introduction

In the previous communications on the activation energy of viscous flow,  $E_\eta$ , for aqueous ethanol solutions,<sup>1-3</sup> it has been shown that  $E_\eta$  exhibits stepwise variation for dilute alcohol and cyclic variation at the other end of the system. In a paper describing the measurements on  $E_\eta$  for 5% and 11% ethanol, the graphical comparison suggested a possible regular shift of corresponding energy jumps, with change in alcohol concentration.<sup>3</sup> In a later communication dealing with the finer study of these discontinuities in  $E_\eta$  from 0 to 30% ethanol, at the concentration intervals of 2%, it was noticed<sup>4</sup> that these shifts are functions of concentration, but are more or less abrupt in certain regions, *e.g.* between 26 to 42°C, especially for 2.5% to 6.9% ethanol solutions.

In an attempt to understand these puzzling phenomena, a study of temperature derivatives of the other physical properties, such as density and refractive index, has been undertaken and are being reported in the present series of papers. The detailed study on the accurate measurements of these derivative at close temperatures established a definite degree of correspondence between these phenomena, but revealed certain anomalies corresponding to some of the jumps observed in  $E_\eta$ .

In Part II of this series,<sup>5</sup> a detailed examination of the concentration dependence of energy jumps from 10°C to 50°C for dilute alcohol was undertaken, and it was noted that (cf. Fig. 3) the movement of these jumps with alcohol concentration are mostly smooth, but with some evidence of branching of these discontinuities into pairs at certain concentrations, accompanied by appearance and disappearance of certain steps. In order to throw further light, a series of experiments on 16.0%, 17.7%, 21.8% and 23.6% dilute ethanol solutions are reported in the present communication, and these, in combination with the published results<sup>2,4,6</sup> for 8.2%, 11%, 13.8% and 20% ethanol, give data at intervals of 2.5% concentration from 8% to 24% ethanol. An attempt is made to obtain a chart showing the broad variation for the temperature of each jump as a function of ethanol concentration on the pattern of that proposed for 0% to 5% alcohol in an earlier communication.

### Experimental Procedure

The measuring technique is the same as adopted in the previously reported experiments on the flow activation energy,  $E_\eta$ , for water, aqueous alcohol<sup>2,4</sup> and hydrocarbons. The values of  $E_\eta$  are calculated from the differential of the Andrade equation, *viz.*



$$\begin{aligned} E\eta/R &= \Delta \ln \eta/\Delta \left(\frac{1}{T}\right) = -T^2 \Delta \ln \eta/\Delta T \\ &= -T^2 \Delta \ln \nu/\Delta T + T^2 \beta \dots \dots (1) \\ &= E\nu/R + \beta T^2, \quad (2) \end{aligned}$$

where  $\nu$  kinematic viscosity =  $\eta/\rho$ , with  $\eta$  = dynamic viscosity and  $\rho$  = the density of substance.

Here  $\beta$  is the coefficient of dilatation, and  $T^2\beta$  forms a slowly varying correction term, which can be applied to the actual data for  $E\nu/R$ . This basic differential technique has several advantages, such as the elimination of the constant of viscometer and the error in the calibration of stop watch, as well as an inherently high accuracy.

Five to six concordant readings for flow time in U-tube viscometer (No. '1', B.S.S. 188) are taken with a calibrated stop watch graduated to 0.1 sec., and read to an accuracy of  $\pm 0.02$  secs. The viscometer is supported in a Townson and Mercer thermostat having a thermistor bridge, giving temperature control to  $\pm 0.001^\circ\text{C}$  or better, and the interval  $\Delta T$ , which is  $1^\circ\text{C}$  in all the subsequent experiments, is measured with the calibrated differential Beckmann thermometer graduated over a six-degree scale. Concentration of the solutions are checked at four to six stages during the whole course of the experiment, by density and viscosity determinations at appropriate temperatures. At higher temperatures, a ballast bottle containing the test liquid is connected to the viscometer and well immersed in the bath, to control the alcohol content by maintaining dynamic vapour-equilibrium.

#### Experiments on 16.0% and 23.6% Dilute Ethanol

The first set of the measurements was carried out with 16% w/w aqueous ethanol solution in the range of  $10^\circ$  to  $50^\circ\text{C}$ , and the mean of  $E/R$  values for heating and cooling sequence is represented by the smooth curve drawn through solid circles of Fig. 1. Table 1(a) contains the overall mean  $E/R$  values together with their r.m.s. deviations for each set of five successive readings, estimated from those of the temperature and the time of flow; these deviations are of the order of  $\pm 0.005$  units of  $(E/R) \div 1000$ . For comparison with these measurements, the corresponding parts of the graphs for 13.8% and 11% ethanol are reproduced from the earlier work and shown (displaced downward by 0.05 and 0.10, respectively) as the full line and broken line curves of Fig. 1.

There is a general similarity of step-wise variation, with average step-length of  $3.8^\circ\text{C}$  and mean drop of the order of nearly 0.11 units of  $(E/R)/1000$ .

For further comparison with the reported data on 20% solution,<sup>4</sup> the viscosity measurements on 23.6% ethanol were undertaken, again with the thermal interval of one degree C. Table 1(b) gives the mean temperatures, Beckmann readings, time of flow and calculated values of  $(E/R) \div 1000$ , together with their r.m.s. deviations (of the order of  $\pm 0.004$ ) obtained from groups of five successive readings covering the full Beckmann scale. The graph drawn through these (triangles) above the chain-line curve of the earlier data for 20% ethanol, represents the mean  $E/R$  values with an upward displaced scale. The succession of steps occurs at the average interval of  $4.0^\circ\text{C}$  with mean depth of 0.12 units (which is 30 time the r.m.s. experimental scatter), while the two largest jumps at  $25^\circ\text{C}$ . and  $36^\circ\text{C}$ . have depths of 0.15 and 0.18 units of  $(E/R) \div 1000$ .

#### Results with 17.7% and 21.8% Ethanol and Discussion

In order to get a more clear picture of the movements of these discontinuities, it was considered worthwhile to complete the relatively large gaps left between 16.6% and 20% as well as 20% and 23.6% by extending the observations over two more solutions. Flow activation energy measurements are performed on 17.7% ethanol solution in the range of  $10^\circ\text{C}$  to  $50^\circ\text{C}$ , and the curve drawn through hollow circles, displaced 0.05 unit above 16.0% solution, in Fig. 1 represents the mean  $E/R$  values plotted against temperature, showing step-wise variation with the mean interval of  $4.3^\circ\text{C}$  and drop of 0.12 units of  $(E/R) \div 1000$ . The actual values for heating and cooling sequences, together with their r.m.s. scatter (which is of the order of 0.005 units of  $(E/R)/1000$ ) are given in the Tables 2(a), and 2(b). Finally, a set of measurements was carried out on 21.8% ethanol solution, but the results are not plotted in Fig. 1, as those for 20% and 23.6% are too close together above  $30^\circ\text{C}$ .

The positions of the energy jumps, and their depths for all these seven concentrations covering the range from 11% to 24% ethanol are collected in Table 3. The temperature positions of the jumps as function of ethanol concentration are plotted in Fig. 2, the jumps being classified as large, medium or small, compared with the mean values of  $\frac{\Delta E/R}{1000} = 0.11 \pm 0.01$ . These are represented in Fig. 2 by circles, triangles and



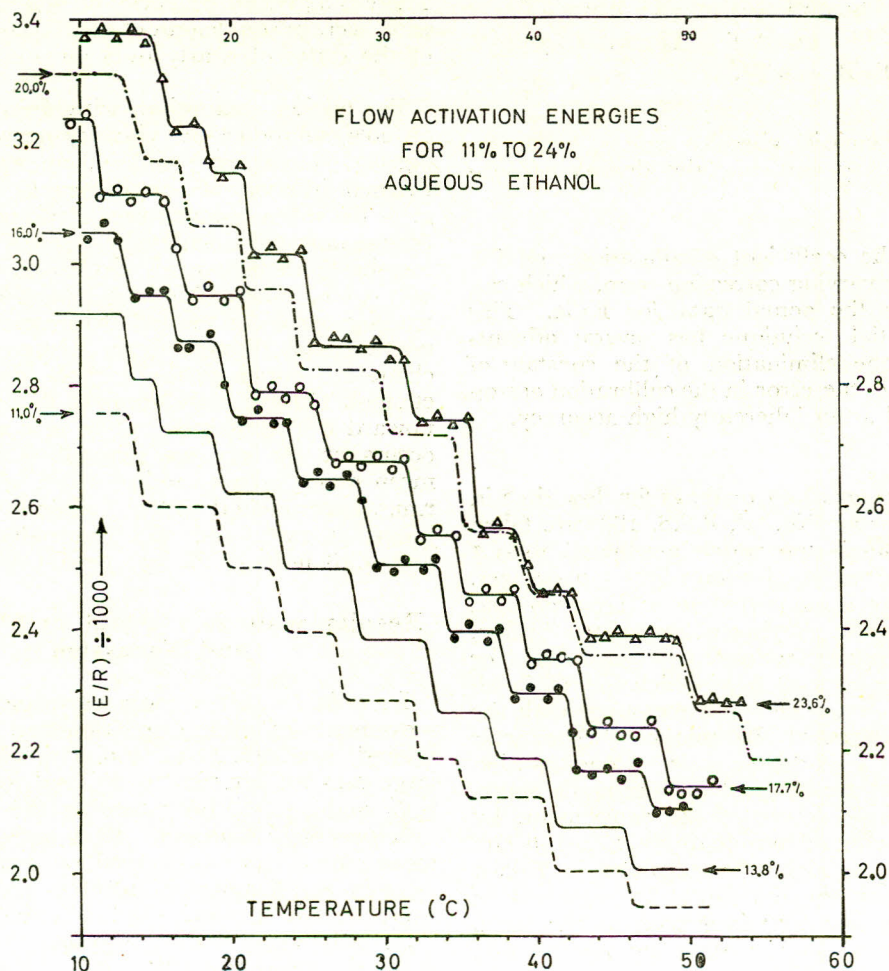


Fig. 1.—Plots of  $(E/R)/1000$ , measured at intervals of one degree C for dilute ethanol solutions containing 11% to 24% ethanol. The vertical scale is correct for the middle graph for 16% ethanol, and successive graphs are shifted up or down by 0.05 unit of  $(E/R)/1000$ . Graphs without plotted points are based on published data.

crosses, respectively, while Fig. 3 is the corresponding chart for 0 to 5% ethanol based on the earlier data of Qureshi and Khan.<sup>5</sup>

It is seen that the various points plotted in Fig. 2 can be connected by smooth curves joining jumps that are of the same order of magnitude. While the region between 11% and 16% is remarkable for the near constancy in temperature of jumps, three branchings are observed in Fig. 2, which indicate the appearance or disappearance of a new jump. The graphs of Fig. 2 are further seen to join very satisfactorily onto those of Fig. 3,

which are reproduced from the earlier experiments performed between 0% and 5% ethanol, using concentrations at the closer intervals of 1%. It is noteworthy that most of the anomalous branchings are to be found at concentrations lower than 6% ethanol. The additional data provided by the extension of the measurements to higher concentrations fills in certain details in the neighbourhood of 5% ethanol, and points out the probable directions for 3 or 4 branchings (shown by arrows) in the region of 3 to 7% ethanol. Further measurements are contemplated to finally decide the behaviour in the three regions marked X, Y and Z in Fig. 3.



TABLE 1 (a).—MEASURED ACTIVATION ENERGIES  $E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T) / 1000$  FOR 16.0%  
AQUEOUS ETHANOL SOLUTION IN THE RANGE OF 10°C. TO 50°C.

Mean tempe- rature °C.	$E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T) / 1000$			Mean Tempe- rature °C.	$E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T) / 1000$		
	Heating sequence	Cooling sequence	Overall mean		Heating sequence	Cooling sequence	Overall mean
10.50	3.051±0.003	3.040±0.003	3.046±0.005	31.50	2.503±0.005	2.517±0.005	2.510±0.007
11.50	3.066±0.003	3.084±0.003	3.075±0.009	32.50	2.497±0.005	2.505±0.005	2.501±0.004
12.50	3.042±0.003	3.047±0.003	3.045±0.003	33.50	2.525±0.005	2.512±0.005	2.518±0.006
13.50	2.952±0.003	2.938±0.003	2.945±0.007	34.50	2.385±0.005	2.392±0.005	2.389±0.003
14.50	2.958±0.003	2.951±0.003	2.955±0.004	35.50	2.408±0.005	2.417±0.005	2.412±0.005
15.50	2.954±0.004	2.967±0.004	2.961±0.006	36.50	2.387±0.005	2.379±0.005	2.383±0.004
16.50	2.862±0.004	2.867±0.004	2.864±0.003	37.50	2.409±0.005	2.396±0.005	2.403±0.007
17.50	2.876±0.004	2.865±0.004	2.870±0.005	38.50	2.287±0.005	2.294±0.005	2.291±0.003
18.50	2.880±0.004	2.888±0.004	2.884±0.004	39.50	2.297±0.005	2.308±0.005	2.302±0.006
19.50	2.811±0.004	2.794±0.004	2.803±0.009	40.50	2.296±0.004	2.290±0.004	2.293±0.003
20.50	2.742±0.004	2.748±0.004	2.745±0.005	41.50	2.300±0.004	2.307±0.004	2.303±0.004
21.50	2.771±0.004	2.755±0.004	2.763±0.008	42.50	2.236±0.004	2.225±0.004	2.231±0.004
22.50	2.741±0.004	2.748±0.004	2.745±0.004	43.50	2.173±0.004	2.168±0.004	2.171±0.003
23.50	2.749±0.004	2.742±0.004	2.746±0.004	44.50	2.162±0.004	2.171±0.004	2.167±0.004
24.50	2.641±0.004	2.648±0.004	2.644±0.004	45.50	2.172±0.005	2.178±0.005	2.175±0.003
25.50	2.662±0.005	2.673±0.005	2.667±0.006	46.50	2.157±0.005	2.152±0.005	2.155±0.003
26.50	2.649±0.005	2.632±0.005	2.640±0.009	47.50	2.170±0.005	2.181±0.005	2.176±0.006
27.50	2.652±0.005	2.662±0.005	2.657±0.005	48.50	2.154±0.004	2.146±0.004	2.150±0.004
28.50	2.614±0.003	2.622±0.003	2.618±0.004	49.50	2.158±0.004	2.153±0.004	2.156±0.003
29.50	2.507±0.003	2.500±0.003	2.503±0.003	50.50	2.159±0.004	2.163±0.004	2.161±0.002
30.50	2.501±0.003	2.496±0.003	2.498±0.003				



TABLE I (b).—BEGMANN READINGS, FLOW TIMES (SECONDS) AND CALCULATED VALUES OF  $E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T)$   
/1000 FOR 23.7% AQUEOUS ETHANOL FROM 10°C. TO 54°C.

Heating sequence						Cooling sequence						Mean E/R $\div$ 1000
Tem- perature °C.	Beckmann reading	Time of flow corrected for level	Mean tem- perature	uncorrect- ed	corrected	Tem- perature °C.	Beckmann reading	Time of flow corrected for level	Mean tem- perature	uncorrect- ed	corrected	
1	2	3	4	5	6	7	8	9	10	11	12	23
10.0	5.116 $\pm$ 0.001	940.38 $\pm$ 0.02				10.0	5.113 $\pm$ 0.000	937.29 $\pm$ 0.02				
			10.50	3.464	3.464 $\pm$ 0.003				10.50	3.471	3.471 $\pm$ 0.003	3.468 $\pm$ 0.004
11.0	4.114 $\pm$ 0.001	900.67 $\pm$ 0.02				11.0	4.120 $\pm$ 0.002	897.98 $\pm$ 0.01				
			11.50	3.468	3.487 $\pm$ 0.003				11.50	3.483	3.484 $\pm$ 0.003	3.486 $\pm$ 0.002
12.0	3.116 $\pm$ 0.000	862.81 $\pm$ 0.01				12.0	3.120 $\pm$ 0.000	860.19 $\pm$ 0.02				
			12.50	3.472	3.472 $\pm$ 0.003				12.50	3.466	3.466 $\pm$ 0.003	3.469 $\pm$ 0.003
13.0	2.114 $\pm$ 0.001	826.79 $\pm$ 0.02				13.0	2.120 $\pm$ 0.001	824.41 $\pm$ 0.02				
			13.50	3.468	3.482 $\pm$ 0.003				13.50	3.482	3.478 $\pm$ 0.003	3.480 $\pm$ 0.002
14.0	1.116 $\pm$ 0.000	792.51 $\pm$ 0.01				14.0	1.124 $\pm$ 0.000	790.33 $\pm$ 0.01				
			14.50	3.452	3.452 $\pm$ 0.003				14.50	3.463	3.463 $\pm$ 0.003	3.458 $\pm$ 0.006
15.0	0.113 $\pm$ 0.000	760.03 $\pm$ 0.01				15.0	0.120 $\pm$ 0.000	759.75 $\pm$ 0.01				
15.0	3.099 $\pm$ 0.001	758.34 $\pm$ 0.02				15.0	3.070 $\pm$ 0.000	759.75 $\pm$ 0.01				
			15.50	3.391	3.396 $\pm$ 0.003				15.50	3.413	3.411 $\pm$ 0.003	3.404 $\pm$ 0.007
16.0	2.093 $\pm$ 0.000	727.86 $\pm$ 0.01				16.0	2.115 $\pm$ 0.002	730.62 $\pm$ 0.03				
			16.50	3.322	3.420 $\pm$ 0.003				16.50	3.311	3.308 $\pm$ 0.003	3.314 $\pm$ 0.006
17.0	1.111 $\pm$ 0.001	700.10 $\pm$ 0.02				17.0	1.094 $\pm$ 0.000	701.74 $\pm$ 0.01				
			17.50	3.315	3.314 $\pm$ 0.003				17.50	3.322	3.321 $\pm$ 0.003	3.317 $\pm$ 0.004
18.0	0.137 $\pm$ 0.000	673.84 $\pm$ 0.02				18.0	0.119 $\pm$ 0.001	673.35 $\pm$ 0.02				
18.0	4.887 $\pm$ 0.001	669.62 $\pm$ 0.02				18.0	4.893 $\pm$ 0.000	669.17 $\pm$ 0.01				
			18.50	3.270	3.270 $\pm$ 0.003				18.50	3.260	3.260 $\pm$ 0.003	3.265 $\pm$ 0.005
19.0	3.813 $\pm$ 0.000	642.54 $\pm$ 0.01				19.0	3.843 $\pm$ 0.001	642.77 $\pm$ 0.02				
			19.50	3.243	3.343 $\pm$ 0.003				19.50	3.238	3.239 $\pm$ 0.003	3.241 $\pm$ 0.002
20.0	2.814 $\pm$ 0.000	618.70 $\pm$ 0.02				20.0	2.856 $\pm$ 0.000	619.22 $\pm$ 0.01				
			20.50	3.253	3.252 $\pm$ 0.003				20.50	3.267	3.266 $\pm$ 0.003	3.259 $\pm$ 0.007
21.0	1.810 $\pm$ 0.000	595.70 $\pm$ 0.01				21.0	1.819 $\pm$ 0.001	595.36 $\pm$ 0.02				
21.0	5.052 $\pm$ 0.001	595.39 $\pm$ 0.02				21.0	5.043 $\pm$ 0.000	595.43 $\pm$ 0.01				
			21.50	3.119	3.117 $\pm$ 0.003				21.50	3.111	3.110 $\pm$ 0.003	3.114 $\pm$ 0.004
22.0	4.000 $\pm$ 0.000	573.30 $\pm$ 0.01				22.0	3.985 $\pm$ 0.001	573.28 $\pm$ 0.02				
			21.50	3.125	3.123 $\pm$ 0.003				22.50	3.126	3.125 $\pm$ 0.003	3.124 $\pm$ 0.001
23.0	3.005 $\pm$ 0.001	553.26 $\pm$ 0.02				23.0	2.992 $\pm$ 0.000	552.27 $\pm$ 0.01				
23.0	4.360 $\pm$ 0.000	554.25 $\pm$ 0.02				23.0	4.360 $\pm$ 0.001	554.27 $\pm$ 0.02				
			23.50	3.095	3.091 $\pm$ 0.004				23.50	3.119	3.114 $\pm$ 0.004	3.102 $\pm$ 0.001
24.0	3.320 $\pm$ 0.001	534.31 $\pm$ 0.03				24.0	3.321 $\pm$ 0.000	534.23 $\pm$ 0.02				
			24.50	3.129	3.127 $\pm$ 0.004				24.50	3.113	3.112 $\pm$ 0.004	3.120 $\pm$ 0.007
25.0	2.297 $\pm$ 0.000	515.35 $\pm$ 0.02				25.0	2.398 $\pm$ 0.001	516.18 $\pm$ 0.03				
			25.50	2.978	2.978 $\pm$ 0.004				25.50	2.958	2.958 $\pm$ 0.004	2.968 $\pm$ 0.010
26.0	1.305 $\pm$ 0.001	498.59 $\pm$ 0.02				26.0	1.362 $\pm$ 0.000	499.71 $\pm$ 0.02				
26.0	4.166 $\pm$ 0.000	501.30 $\pm$ 0.01				26.0	4.168 $\pm$ 0.000	501.24 $\pm$ 0.02				
			26.50	2.967	2.967 $\pm$ 0.003				26.50	2.981	2.981 $\pm$ 0.003	2.974 $\pm$ 0.007
27.0	3.170 $\pm$ 0.001	485.07 $\pm$ 0.02				27.0	3.196 $\pm$ 0.001	485.32 $\pm$ 0.01				
			27.50	2.971	2.970 $\pm$ 0.003				27.50	2.980	2.980 $\pm$ 0.003	2.975 $\pm$ 0.005
28.0	2.125 $\pm$ 0.000	468.66 $\pm$ 0.01				28.0	2.116 $\pm$ 0.000	468.36 $\pm$ 0.02				
			28.50	2.951	2.952 $\pm$ 0.003				28.50	2.965	2.966 $\pm$ 0.003	2.959 $\pm$ 0.007
29.0	1.095 $\pm$ 0.000	453.26 $\pm$ 0.02				29.0	1.126 $\pm$ 0.000	453.49 $\pm$ 0.01				
			29.50	2.976	2.976 $\pm$ 0.003				29.50	2.965	2.965 $\pm$ 0.003	2.970 $\pm$ 0.005
30.0	0.058 $\pm$ 0.001	438.21 $\pm$ 0.02				30.0	0.069 $\pm$ 0.001	438.24 $\pm$ 0.02				

(Continued)



(TABLE I (b) Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
30.0	4.044±0.000	438.80±0.02										
			30.50	2.943	2.946±0.004							
31.0	2.998±0.001	424.26±0.02										
			31.50	2.941	2.942±0.004							
32.0	1.965±0.000	410.72±0.01										
			32.50	2.844	2.843±0.004							
33.0	0.963±0.001	398.39±0.02										
			33.50	2.867	2.863±0.004							
34.0	2.154±0.001	386.29±0.02										
			34.50	2.835	2.834±0.004							
35.0	1.154±0.000	374.89±0.01										
			35.50	2.847	2.847±0.004							
36.0	0.173±0.001	364.06±0.02										
36.0	4.500±0.000	363.65±0.01										
			36.50	2.666	2.666±0.004							
37.0	3.483±0.001	353.54±0.02										
			37.50	2.662	2.667±0.004							
38.0	2.475±0.000	343.84±0.01										
			38.50	2.656	2.654±0.004							
39.0	1.465±0.001	334.47±0.01										
			39.50	2.601	2.605±0.004							
40.0	0.463±0.002	325.67±0.03										
40.0	5.092±0.002	324.57±0.03										
			40.50	2.569	2.560±0.005							
41.0	4.065±0.000	316.01±0.02										
			41.50	2.561	2.560±0.005							
42.0	3.089±0.001	308.13±0.02										
			42.50	2.566	2.562±0.005							
43.0	2.082±0.000	300.24±0.01										
			43.50	2.482	2.482±0.005							
44.0	1.065±0.001	292.78±0.02										
44.0	5.453±0.000	291.57±0.02										
			44.50	2.488	2.488±0.005							
45.0	4.451±0.001	284.45±0.01										
			45.50	2.491	2.492±0.005							
46.0	3.475±0.000	277.72±0.02										
			46.50	2.479	2.479±0.005							
47.0	2.501±0.001	271.24±0.02										
47.0	4.894±0.001	270.28±0.02										
			47.50	2.492	2.492±0.006							
48.0	3.871±0.000	263.66±0.01										
			48.50	2.484	2.482±0.006							
49.0	2.872±0.001	257.41±0.02										
			49.50	2.474	2.470±0.006							
50.0	1.893±0.000	251.49±0.02										
50.0	5.028±0.001	251.71±0.02										
			50.50	2.369	2.370±0.006							
51.0	4.026±0.001	246.08±0.02										
			51.50	2.381	2.382±0.006							
52.0	3.029±0.000	240.60±0.01										
			52.50	2.379	2.380±0.006							
53.0	2.021±0.001	235.22±0.02										
			53.50	2.372	2.373±0.006							
54.0	1.029±0.000	230.09±0.01										
			54.0	1.034±0.001	230.02±0.02							



TABLE 2 (a).—MEASURED ACTIVATION ENERGIES  $E/R \div 1000 = -T^2(\Delta \ln v / \Delta T) / 1000$  FOR 17.7% AQUEOUS ETHANOL SOLUTION IN THE RANGE OF 9°C TO 52°C.

*Temperature °C.	$E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T) 1000$			Temperature °C.	$E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T) 1000$		
	Heating sequence	Cooling sequence	Overall mean		Heating sequence	Cooling sequence	Overall mean
9.50	3.276±0.003	3.285±0.003	3.280±0.005	31.50	2.730±0.004	2.721±0.004	2.725±0.005
10.50	3.301±0.003	3.289±0.003	3.295±0.006	32.50	2.594±0.004	2.606±0.004	2.600±0.006
11.50	3.157±0.003	3.164±0.003	3.161±0.003	33.50	2.613±0.004	2.608±0.004	2.610±0.003
12.50	3.179±0.003	3.171±0.003	3.175±0.004	34.50	2.601±0.004	2.610±0.004	2.605±0.004
13.50	3.153±0.003	3.158±0.003	3.156±0.002	35.50	2.491±0.004	2.503±0.004	2.496±0.004
14.50	3.177±0.003	3.166±0.003	3.171±0.005	36.50	2.517±0.005	2.510±0.005	2.514±0.004
15.50	3.151±0.004	3.160±0.004	3.156±0.004	37.50	2.501±0.005	2.495±0.005	2.498±0.003
16.50	3.083±0.004	2.072±0.004	3.077±0.005	38.50	2.508±0.005	2.525±0.005	2.516±0.008
17.50	2.983±0.004	2.997±0.004	2.990±0.007	39.50	2.453±0.005	2.443±0.005	2.448±0.005
18.50	3.018±0.004	3.010±0.004	3.014±0.004	40.50	2.461±0.005	2.450±0.005	2.455±0.006
19.50	2.993±0.004	2.998±0.004	2.996±0.002	41.50	2.450±0.004	2.456±0.004	2.453±0.003
20.50	2.999±0.005	2.990±0.005	2.995±0.005	42.50	2.452±0.004	2.447±0.004	2.450±0.003
21.50	2.841±0.005	2.833±0.005	2.837±0.005	43.50	2.274±0.004	2.285±0.004	2.280±0.005
22.50	2.840±0.005	2.855±0.005	2.848±0.008	44.50	2.293±0.004	2.306±0.004	2.299±0.007
23.50	2.827±0.006	2.834±0.005	2.831±0.004	45.50	2.281±0.004	2.273±0.004	2.277±0.004
24.50	2.850±0.004	2.844±0.004	2.847±0.003	46.50	2.272±0.005	2.285±0.005	2.278±0.007
25.50	2.818±0.004	2.825±0.004	2.822±0.004	47.50	2.302±0.005	2.298±0.005	2.300±0.002
26.50	2.729±0.004	2.721±0.004	2.725±0.004	48.50	2.196±0.005	2.185±0.005	2.191±0.006
27.50	2.733±0.004	2.728±0.004	2.731±0.003	49.50	2.178±0.006	2.186±0.005	2.182±0.004
28.50	2.714±0.004	2.721±0.004	2.718±0.004	50.50	2.189±0.006	2.176±0.006	2.183±0.007
29.50	2.723±0.004	2.729±0.004	2.726±0.003	51.50	2.195±0.006	2.186±0.006	2.190±0.005
30.50	2.725±0.004	2.710±0.004	2.718±0.008				

TABLE 2 (b).—MEASURED ACTIVATION ENERGIES  $E/R \div 1000 = -T^2(\Delta \ln v / \Delta T) / 1000$  FOR 21.8% AQUEOUS ETHANOL IN THE RANGE OF 10°C TO 54°C AT THE INTERVAL OF 1°C.

Temperature °C.	$E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T) 1000$			Temperature °C.	$E/R \div 1000 = -T^2 (\Delta \ln v / \Delta T) 1000$		
	Heating sequence	Cooling sequence	Overall mean		Heating sequence	Cooling sequence	Overall mean
10.50	3.407±0.003	3.420±0.003	3.414±0.006	32.50	2.820±0.004	2.829±0.004	2.824±0.004
11.50	3.409±0.003	3.402±0.003	3.405±0.003	33.50	2.831±0.004	2.824±0.004	2.827±0.004
12.50	3.424±0.003	3.417±0.003	3.421±0.004	34.50	2.812±0.004	2.829±0.004	2.821±0.009
13.50	3.351±0.003	3.364±0.003	3.357±0.005	35.50	2.600±0.003	2.669±0.003	2.675±0.007
14.50	3.358±0.003	3.351±0.003	3.354±0.004	36.50	2.676±0.003	2.682±0.003	2.679±0.003
15.50	3.270±0.003	3.279±0.003	3.275±0.004	37.50	2.660±0.003	2.852±0.083	2.656±0.004
16.50	3.297±0.003	3.291±0.003	3.294±0.003	38.50	2.692±0.003	2.681±0.003	2.687±0.005
17.50	3.218±0.003	3.207±0.003	3.212±0.006	39.50	2.563±0.003	2.548±0.003	2.555±0.008
18.50	3.200±0.003	3.205±0.003	3.203±0.003	40.50	2.578±0.005	2.573±0.005	2.575±0.003
19.50	3.219±0.003	3.232±0.003	3.225±0.007	41.50	2.557±0.005	2.550±0.005	2.554±0.004
20.50	3.158±0.004	3.165±0.004	3.162±0.004	42.50	2.552±0.005	2.563±0.005	2.558±0.005
21.50	3.110±0.004	3.099±0.004	3.105±0.005	43.50	2.509±0.005	2.502±0.005	2.505±0.003
22.50	3.123±0.004	3.130±0.004	3.126±0.003	44.50	2.476±0.005	2.463±0.005	2.470±0.007
23.50	3.098±0.004	3.109±0.004	3.103±0.006	45.50	2.466±0.005	2.462±0.005	2.464±0.002
24.50	3.029±0.004	3.017±0.004	3.023±0.006	46.50	2.501±0.005	2.489±0.005	2.495±0.006
25.50	3.031±0.004	3.020±0.004	3.025±0.006	47.50	2.458±0.005	2.465±0.005	2.462±0.003
26.50	2.972±0.004	2.977±0.004	2.975±0.003	48.50	2.483±0.005	2.476±0.005	2.480±0.004
27.50	2.928±0.004	2.923±0.004	2.925±0.003	49.50	2.431±0.005	2.442±0.005	2.436±0.006
28.50	2.915±0.004	2.922±0.004	2.918±0.004	50.50	2.384±0.005	2.376±0.005	2.380±0.004
29.50	2.939±0.004	2.929±0.004	2.934±0.005	51.50	2.599±0.005	2.586±0.005	2.433±0.007
30.50	2.925±0.004	2.934±0.005	2.929±0.004	52.50	2.493±0.005	2.496±0.005	2.495±0.003
31.50	2.907±0.004	2.904±0.004	2.905±0.002	53.50	2.482±0.005	2.475±0.005	2.476±0.000



TABLE 3.—SYNOPSIS OF THE OBSERVED TEMPERATURES (IN °C.) AT THE JUMPS OF  $(E/R)/1000$ , TOGETHER WITH THE MAGNITUDES OF THESE JUMPS FOR VARIOUS AQUEOUS ETHANOL SOLUTIONS FROM 11.0% TO 23.6% ETHANOL.

11.0% ethanol	1. Temperature at jump	13.8	—	19.2	23.3	27.1	32.0	35.1	40.8	46.0
	2. Depth of jump	0.16	—	0.10	0.11	0.11	0.10	0.07	0.12	0.06
13.8% ethanol	1. Temperature at jump	13.2	15.1	19.2	23.1	28.1	33.1	37.1	40.9	46.0
	2. Depth of jump	0.11	0.08	0.10	0.12	0.11	0.12	0.07	0.11	0.07
16.0% ethanol	1. Temperature at jump	13.0	16.1	19.6	24.0	28.9	33.8	37.9	42.4	47.3
	2. Depth of jump	0.10	0.08	0.12	0.10	0.14	0.11	0.10	0.13	0.07
17.7% ethanol	1. Temperature at jump	11.1	16.4	21.0	25.9	32.0	34.8	39.2	43.0	48.5
	2. Depth of jump	0.12	0.16	0.16	0.11	0.12	0.09	0.10	0.11	0.10
20.0% ethanol	1. Temperature at jump	13.6	16.9	20.8	24.2	30.0	34.8	39.0	42.6	49.9
	2. Depth of jump	0.14	0.11	0.10	0.13	0.11	0.15	0.10	0.10	0.10
21.8% ethanol	1. Temperature at jump	14.1	17.2	20.7	25.2±1.4	31.7	35.1	39.0	43.2	49.9
	2. Depth of jump	0.13	0.07	0.10	0.18*	0.11	0.15	0.11	0.09	0.09
23.6% ethanol	1. Temperature at jump	15.4	18.4	21.1	25.2	31.6	36.0	39.4	43.0	50.1
	2. Depth of jump	0.15	0.07	0.13	0.15	0.12	0.18	0.09	0.08	0.11

Note.—There is some anomaly in the region of 23°C to 27°C in case of 21.8% ethanol solution, which shows two jumps close together, instead of the single one at 25°C in the case of the 20.0% and 23.6% solutions.

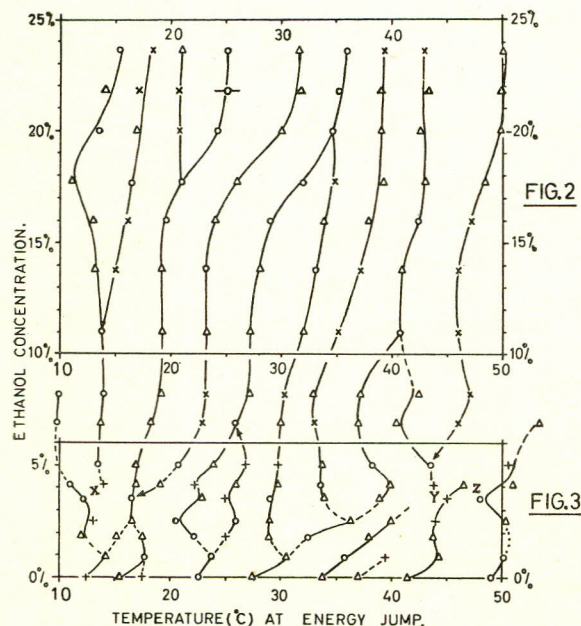


Fig. 2.—Chart showing plots of the temperatures at the various minima observed in the activation energy for the seven solutions in the range of 11% to 24% ethanol. The circles, triangles and crosses correspond respectively to jumps that are classified as large, medium or small, on the basis of comparison with the mean value of 0.11 for  $\Delta(E/R)/1000$ . It is seen that a smooth set of graphs can be drawn passing through these plotted points. The region between 11% and 16% is remarkable for the near constancy of the temperatures for most of the jumps.

Fig. 3.—It is reproduced directly below Fig. 2 from the previously published data of Qureshi and Khan, and the temperatures of the minima for two intermediate solutions *viz.* 6.9% and 8.2% ethanol (previously reported by Ahsanullah and Qurashi) are also plotted between these two Figs. 2 and 3. With the help of these intermediate points, the series of graphs in Figs. 2 and 3 are found to fit smoothly into each other.



It is to be noted that the graphs of Figs. 2 and 3 generally bear out the earlier conjectures<sup>4</sup> regarding the definite dependence of the energy jumps on ethanol concentration, but in addition point to the presence of some significant structural changes associated with the branching out of two jumps from a single one. The appearance and growth of these subsidiary activation energy jumps is an intriguing phenomenon in itself, and it is hoped to make a finer study of this, with particular reference to the very dilute solutions below 5% ethanol.

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